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SUN RULES FOR OPTICAL EXTINCTION AND SCATTERING BY
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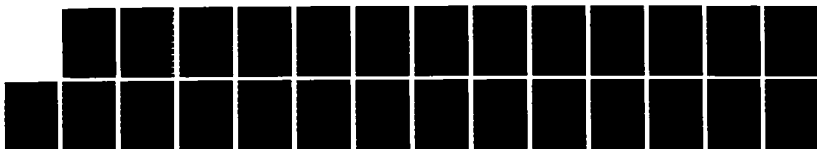
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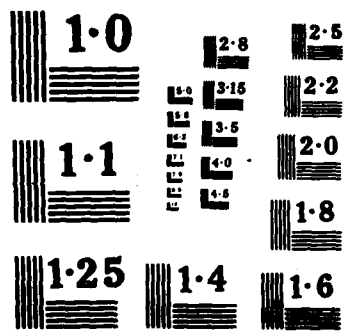
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Sum Rules for Optical Extinction and Scattering
by Small Particles

Annual Report for 1985

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1. INTRODUCTION

A central problem in developing effective smoke obscurants for space applications is to maximize volumetric extinction or absorption at the wavelength of the incident electromagnetic radiation. Yet this is a problem without a general solution. There are an enormous number of different kinds of obscuring particles: they may vary in composition, shape, and size. To choose a combination of particles that will give the greatest obscuration over the largest possible wavelength interval by doing detailed calculations for all possible particles--even if the necessary analytical tools were available--would be an endless undertaking. Nevertheless, it is possible to make recommendations based on very general considerations. One can establish bounds not on extinction at any wavelength, but rather extinction integrated over all wavelengths, by invoking sum rules.

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MATTHEW J. KERPER

Chief, Technical Information Division

2. SUM RULES FOR EXTINCTION

2.1 General Considerations

Sum rules follow from very general relations called dispersion or Kramers-Kronig relations. Consider two time-dependent physical quantities, which we may call the input and the output; the corresponding Fourier transforms, which are complex functions of frequency ω , are denoted by $X_i(\omega)$ and $X_o(\omega)$. If the relation between these two transforms is linear



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$$X_o(\omega) = R(\omega)X_i(\omega),$$

and causal (the output cannot precede the input in time), then the real and imaginary parts of the response function $R(\omega)$ are connected by integral relations (subject to restrictions on the asymptotic behavior of R).

Although dispersion relations are important in elementary particle physics (e.g., Goldberger, 1960) and some areas of optics, particularly optical properties of solids (e.g., Stern, 1963), they have been largely ignored by workers in the field of absorption and scattering of light by small particles. One exception is the work of Purcell (1969), which has received little attention. Box and McKellar (1978) derived an expression for integrated extinction similar to Purcell's but from a completely different point of view. Recently, Purcell's results were rederived and extended by McKellar, Box, and Bohren (1982), and an alternative treatment was given by Bohren and Huffman (1983, p. 116). This treatment is outlined below because it will form the basis for further investigation.

Consider a single particle illuminated by a plane, monochromatic wave of frequency ω and wavenumber k propagating in the z direction. At sufficiently large distances r from the particle, the electric field \underline{E}_s scattered by it is transverse and is given asymptotically by

$$\underline{E}_s \sim \frac{e^{ik(r-z)}}{-ikr} \underline{E}_i^X, \quad kr \gg 1 \quad (1)$$

where the incident field (polarized in the x direction) \underline{E}_i is $E\hat{e}_x$ and $E = E_0 \exp(ikz - i\omega t)$. The vector scattering amplitude \underline{X} in the forward direction determines the extinction cross section C_{ext} through the optical theorem

$$C_{\text{ext}} = \frac{4\pi}{k^2} \text{Re}\{S(0)\}, \quad (2)$$

where $S(0)$ is the projection of the forward scattering amplitude onto the direction of polarization of the incident beam.

Because the relation (1) is linear and causal (the scattered wave cannot precede the incident wave in time), the real and imaginary parts of $S(0)$ are connected by integral relations. However, the asymptotic behavior of $S(0)$ is such that it is not $S(0)$ itself that satisfies these relations but rather a suitable modification of it. For integral relations to exist, $S(0)$ must vanish in the limit of infinite frequency. But it follows from Fraunhofer diffraction theory that for sufficiently high frequencies

$$S(0) = \frac{\omega^2}{4\pi c^2} 2G, \quad (3)$$

where c is the speed of light in vacuo and G is the geometrical cross sectional area projected onto the incident beam (for a sphere of radius a , $G = \pi a^2$). The function F formed from S

$$F(\omega) = \frac{S(0)}{\omega^2} - \frac{2G}{4\pi c^2} \quad (4)$$

vanishes in the limit of infinite frequency; if $S(0)$ is analytic in the top half of the complex frequency plane (this is required by causality) and decreases at least as ω^2 at low frequencies, then F is also analytic, hence its real (F') and imaginary (F'') parts are connected by the dispersion relations

$$F'(\omega) = \frac{2}{\pi} P \int_0^{\infty} \frac{\Omega F''(\Omega)}{\Omega^2 - \omega^2} d\Omega, \quad (5)$$

$$F''(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{F'(\Omega)}{\Omega^2 - \omega^2} d\Omega, \quad (6)$$

where P denotes the Cauchy principal value of the integrals.

If we now substitute (2) in (6), we obtain the dispersion relation satisfied by the extinction cross section

$$P \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega = -2\pi^2 c^2 \frac{\text{Im}\{S(0)\}}{\omega^2}. \quad (7)$$

It is tempting to take the limit of (7) as the frequency goes to zero and write

$$\lim_{\omega \rightarrow 0} P \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega = \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2} d\Omega = -2\pi^2 c^2 \lim_{\omega \rightarrow 0} \frac{\text{Im}\{S(0)\}}{\omega^2}. \quad (8)$$

Indeed, this is what has been done previously. But underlying (8) are some implicit assumptions that we must now investigate.

2.2 Requirements on the behavior of C_{ext} at low frequencies

Let us suppose that the limit of the right side of (7) as

the frequency goes to zero exists. This means that the limit of the left side also exists, but it does not necessarily follow that this limit is

$$\int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2} d\Omega \quad (9)$$

The Cauchy principal value is also obtained as a limit, and the order of limits cannot always be interchanged. Suppose, for example, that C_{ext} were a constant. Since C_{ext} is inherently positive, it follows that (9) diverges because the integral of $1/\Omega^2$ over any region containing the origin diverges. Thus, it is clear that there must be restrictions on the low frequency behavior of C_{ext} in order for (8) to be valid. For simplicity, let us assume that C_{ext} is proportional to the frequency squared at low frequencies. What we want to prove is that

$$\lim_{\omega \rightarrow 0} P \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega = \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2} d\Omega . \quad (10)$$

From the definition of the Cauchy principal value, the left side of (10) is

$$\lim_{\omega \rightarrow 0} \lim_{\delta \rightarrow 0} \left(\int_0^{\omega - \delta} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega + \int_{\omega + \delta}^{\beta} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega + \int_{\beta}^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega \right) \quad (11)$$

We can make ω and δ as small as we wish (but not zero) subject to the requirement that $\omega > \delta$. The upper limit of integration β

can also be made as small as we wish subject to the requirement that it is greater than $\omega + \delta$. If C_{ext} is proportional to the frequency squared at sufficiently low frequencies, then we can substitute the low frequency expression in the first two integrals in (11). These integrals can now be evaluated, and both limits taken. The result is (10). Thus, if C_{ext} decreases as the frequency squared in the limit of zero frequency, (8) is valid. This requirement is more stringent than it need be. All that is required is that at low frequencies C_{ext} decrease as frequency to the power $1 + \sigma$, where σ is any positive number.

At sufficiently low frequencies, the extinction cross section of an ellipsoid composed of either a simple free electron metal or a simple insulator is proportional to frequency squared (see, e.g., Bohren and Huffman, 1983, pp. 345 and 348). Thus, the low frequency behavior of C_{ext} for real particles is such that (8) is valid.

It also follows from the preceding analysis that there do not exist sum rules for the extinction cross section with any form other than (9). For example, suppose we inquire into the existence of a sum rule for the quantity ωC_{ext} . The low frequency limit of this quantity is such that we may interchange the order of limits; that is,

$$\lim_{\omega \rightarrow 0} P \int_0^{\infty} \frac{\Omega C_{\text{ext}}(\Omega)}{\Omega^2 - \omega^2} d\Omega = \int_0^{\infty} \frac{C_{\text{ext}}(\Omega)}{\Omega} d\Omega.$$

Now, however, C_{ext} does not have the proper behaviour at high frequencies; that is, ωF does not vanish in the limit of

infinite frequency, which is required for the validity of the integral relations (5) and (6). The same argument holds for any quantity of the form $\omega^n C_{\text{ext}}$, where n is any number other than 0. Thus, we conclude that only one sum rule for C_{ext} exists.

2.3 Sum rules when magnetic dipole terms are included

To proceed further we need to determine the limit on the right side of (8), that is, we need to know the low-frequency limit of the forward scattering amplitude. For particles composed of an electrical insulator, this amplitude will be that given by electrostatics, i.e., the electric dipole term in a multipole expansion of the electromagnetic field scattered by the particle. But for metallic particles, it is not clear if this choice is correct: at far infrared frequencies, the magnetic dipole term can be equal to or even greater than the electric dipole term. For this reason, the role of the magnetic dipole term in sum rules was investigated.

In order to apply Rayleigh theory (i.e., electrostatics) to scattering by small particles, two conditions must be satisfied: the size parameter $x = 2\pi a/\lambda$, where a is a characteristic linear dimension of the particle, must be small compared with unity as must $|m|x$, where m is the particle's complex refractive index. Let us consider a simple free-electron metal, the dielectric function of which is given by the Drude formula

$$\epsilon = \epsilon' + i\epsilon'' = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (12)$$

where ω_p is the plasma frequency (typically in the ultraviolet) and γ is a damping factor, which also has the dimensions of frequency. The refractive index is the square root of ϵ . The size parameter x can be written as

$$x = \frac{\omega a}{c}, \quad (13)$$

from which it is clear that x vanishes in the limit of zero frequency. But since $|m|$ does not vanish in this limit for a material described by (12), it is not obvious that $|m|x$ does. The modulus of the refractive index is

$$|m| = (\epsilon'^2 + \epsilon''^2)^{1/4}. \quad (14)$$

For frequencies ω much less than γ , and subject to the requirement that $\gamma \ll \omega_p$, we can combine (12)-(14) to obtain

$$|m|x \approx \frac{\omega_p a}{c} \sqrt{\omega/\gamma} \quad \omega \ll \gamma \ll \omega_p \quad (15)$$

Thus, provided that γ is not identically zero, $|m|x$ also vanishes in the limit of zero frequency. This condition on γ is equivalent to requiring the dc conductivity ω_p^2/γ to be finite.

To proceed further, we must consider a specific particle. The forward scattering amplitude for a sphere is an infinite series in the scattering coefficients a_n and b_n :

$$S(0) = \frac{1}{2} \sum (2n+1)(a_n + b_n) \quad (16)$$

For sufficiently small x and $|m|x$, the electric dipole term a_1 and the magnetic dipole term b_1 dominate the series (16) and are given approximately by

$$a_1 = -i \frac{2x^3}{3} \frac{\epsilon - 1}{\epsilon + 2} \quad b_1 = -i \frac{x^5}{45} (\epsilon - 1) \quad (17)$$

If γ is not identically zero, then for a material with dielectric function (12)

$$\lim_{\omega \rightarrow 0} b_1/a_1 = 0 \quad (18)$$

On physical grounds, we expect (18) to be valid for particles of arbitrary shape. Thus, we have established that the sum rule (8) is valid even for metallic particles and that the scattering amplitude in the zero frequency limit corresponds to electric dipole radiation, provided only that the dc conductivity is finite.

Before proceeding, we need to consider the consequences of mean free path limitations for sum rules.

2.4 Limitation of the mean free path

It will again be useful to consider a specific particle, a sphere. We also define the volumetric attenuation coefficient α_v as the extinction cross section per unit particle volume. It follows from (8), (16), and (17) that the volumetric attenuation

coefficient is independent of particle size and depends only on the low frequency limit of the dielectric function

$$\int_0^{\infty} \alpha_v d\lambda = 3\pi^2 \lim_{\omega \rightarrow 0} \operatorname{Re} \left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \right). \quad (19)$$

We have also transformed the variable of integration from frequency to wavelength. For a material with dielectric function (12), the term on the right side of (19) is

$$\operatorname{Re} \left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \right) = \frac{-\omega_p^2 (3\omega^2 - \omega_p^2)}{(3\omega^2 - \omega_p^2)^2 + 9\gamma^2 \omega^2}. \quad (20)$$

The limit of (20) as the frequency goes to zero is unity, regardless of the value of γ , and in this instance

$$\int_0^{\infty} \alpha_v d\lambda = 3\pi^2. \quad (21)$$

The damping term γ arises from scattering of electrons by the lattice, electron-phonon scattering. If it were not for electron-phonon scattering, the dc conductivity of a metal would be infinite. In a sufficiently small particle, scattering of electrons by its boundary may be more important than scattering by the lattice. That is, the mean free path for scattering by the boundary may be less than that for scattering by a phonon. This was first pointed out by Doyle (1958), and subsequently investigated by Doremus (1964), Kreibig and von Fragstein (1969), Kreibig (1974), and Granqvist and Hunderi (1977). Kreibig (1974) interpreted absorption by small silver particles

by modifying the damping constant in the Drude expression (12). This damping constant, which is the inverse of the collision time for conduction electrons, is increased because of additional collisions with the boundary of the particle. Under the assumption that the electrons are diffusely reflected at its boundary, can be written

$$\gamma = \gamma_{\text{bulk}} + v_F/L, \quad (22)$$

where γ_{bulk} is the bulk metal damping constant, v_F is the electron velocity at the Fermi surface, and L is the effective mean free path for collisions with the boundary. Kreibig took L to be $4a/3$ for a sphere of radius a . We have already shown, however, that (21) is independent of γ . Thus, we conclude that the limitation of the electron mean free path by the boundaries of a small particle do not affect its integrated extinction. Detailed calculations for spheres (see Bohren and Huffman, 1983, p. 338) are in accord with this conclusion. When particles are sufficiently small, the effect of their boundaries is to decrease peak extinction while simultaneously broadening it in such a way that integrated extinction remains constant.

3. SUM RULES FOR PARTICLES OF VARIOUS SHAPES

3.1 A general result and its interpretation

The scattering amplitude $S(0)$ for any particle that is

sufficiently small compared with the wavelength of the light illuminating it is proportional to its volume. Thus, it follows from (8) that integrated extinction per unit volume of any particle is independent of its size: it depends only on its composition. When a particle is illuminated by an electromagnetic wave, various electromagnetic modes may be excited. The larger the particle, the greater the number of such modes. This follows from simple physical reasoning, although it is also evident from exact solutions to scattering problems. The smaller the particle, the fewer the modes that can be excited. Yet integrated extinction is independent of particle size. That is, a fixed amount of total extinction must be shared by modes, the number of which increases with increasing particle size. Thus, the larger the particle, the more a fixed amount of total extinction has to be shared with an ever larger number of modes. Hence the extinction associated with each resonant mode must decrease with increasing size. This in turn implies that the smallest particles have the greatest extinction. This is a very general result. It can be verified in specific instances. For example, the greatest possible extinction per unit volume of a sphere is obtained for spheres much smaller than the wavelength. This high volumetric extinction, however, is concentrated in a narrow spectral band, as implied by the sum rule.

3.2 Ellipsoidal particles

Equation (8) is completely general. To apply it to a definite particle requires the scattering amplitude in the forward direction in the limit of zero frequency. Consider a homogeneous ellipsoidal particle of volume v illuminated by light polarized along one of its principal axes. At sufficiently low frequencies, this particle is equivalent to a dipole with (induced) moment

$$\underline{p} = \epsilon_m v \frac{\epsilon - 1}{1 + L(\epsilon - 1)} \underline{E}_0 \quad (23)$$

where \underline{E}_0 is the incident field, L is a geometrical factor lying between 0 and 1, and ϵ_m is the permittivity of the surrounding medium (assumed to be nonabsorbing). In general, there is a distinct geometrical factor L_j for each of the three principal axes of the ellipsoid, the sum of which is unity. In general, the incident light is not polarized along one of the principal axes, so we have to resolve the incident electric field into its components along the principal axes of the ellipsoid. We denote these coordinate axes, which are fixed relative to the particle, by xyz . Axes relative to which the incident light is specified (laboratory coordinate system) are denoted by $x'y'z'$. If the incident light is polarized along the x' axis, the scattering amplitude corresponding to (23) is

$$\underline{X} = \frac{ik^3}{4\pi\epsilon_m} \frac{\hat{\underline{e}}_r \times (\hat{\underline{e}}_r \times \underline{p})}{E_{0x'}} \quad (24)$$

where $\hat{\underline{e}}_r$ is a unit vector in the scattering direction. The

projection of (24) onto the x' axis in the forward direction is

$$S(0) = -\frac{ik^3}{4\pi} \alpha'_{11},$$

where

$$\alpha'_{11} = \alpha_1 a_{11}^2 + \alpha_2 a_{21}^2 + \alpha_3 a_{31}^2,$$

$$\alpha_j = v \frac{\epsilon - 1}{1 + L_j(\epsilon - 1)}. \quad (25)$$

The quantities a_{11} etc. are direction cosines between the primed and unprimed axes, and they satisfy

$$a_{11}^2 + a_{21}^2 + a_{31}^2 = 1$$

If we combine substitute (25) in (18) we obtain the sum rule

$$\int_0^\infty \frac{C_{\text{ext}}(\Omega)}{\Omega^2} d\Omega = \frac{\pi v}{2C} \lim_{\omega \rightarrow 0} \text{Im} \left[i \sum_{j=1}^3 a_{j1}^2 \frac{\epsilon - 1}{1 + L_j(\epsilon - 1)} \right]. \quad (26)$$

As a check on (26), we note that it reduces to (19) when all the geometrical factors are equal (i.e., the ellipsoid is a sphere) and the variable of integration is changed from frequency to wavelength.

A less general, but more useful, form of (26) is obtained by averaging over all orientations of the ellipsoid. Unless special care is taken, a cloud of ellipsoidal particles is likely to be randomly oriented, in which instance

$$\langle a_{11}^2 \rangle = \langle a_{21}^2 \rangle = \langle a_{31}^2 \rangle = \frac{1}{3},$$

where the brackets indicate an average over all directions with equal probability per unit solid angle. The corresponding volumetric attenuation coefficient satisfies

$$\int_0^\infty \alpha_v d\lambda = \pi^2 \lim_{\omega \rightarrow 0} \operatorname{Re} \left(\sum_{j=1}^3 \frac{\epsilon - 1}{3 + 3L_j(\epsilon - 1)} \right) \quad (27)$$

where $\alpha_v = \langle C_{\text{ext}} \rangle / v$. Again, this reduces to (19) when all the geometrical factors are equal.

Each term in the sum on the right side of (27) has the form

$$\lim_{\omega \rightarrow 0} \frac{(\epsilon' - 1)(3 + 3L_j\epsilon' - 3L_j) + 3L_j\epsilon'^{-2}}{(3 + 3L_j\epsilon' - 3L_j)^2 + 9L_j^2\epsilon'^{-2}} \quad (28)$$

Let us consider the low frequency limit of (28) for two classes of materials, metals and polar insulators. The Drude dielectric function (28) applies to an ideal free-electron metal. The imaginary part of this dielectric function goes to infinity in the limit of zero frequency. Hence, for an ideal free-electron metal (27) becomes

$$\int_0^\infty \alpha_v d\lambda = \frac{\pi^2}{3} \sum_{j=1}^3 \frac{1}{L_j}. \quad (29)$$

Now consider an insulator, one for which the imaginary part of the dielectric function goes to zero in the low-frequency limit. For such a material (28) is

$$\lim_{\omega \rightarrow 0} \frac{\epsilon' - 1}{3 + 3L_j \epsilon' - 3L_j} \quad (30)$$

Thus, if

$$L_j \gg \lim_{\omega \rightarrow 0} 1/(\epsilon' - 1) \quad (j = 1, 2, 3), \quad (31)$$

integrated volumetric extinction is still given (approximately) by (29).

All the geometrical factors L_j for a sphere are 1/3. The low-frequency limit of the dielectric function of water is more than 80. Thus, we obtain the unexpected result that integrated extinction by a water droplet is (approximately) that same as that by an equal-volume metallic sphere. The extinction spectra of these two particles are markedly different, and yet the integrals of these spectra are the same. This similarity is not maintained for all shapes. As the particle shape deviates more from sphericity, at least one of the geometrical factors L_j must decrease to the point where (31) is no longer satisfied. Nevertheless, for a wide range of shapes integrated (volumetric) extinction by metallic particles is approximately equal to that of insulating particles made of a substance with a high dielectric at low frequencies function (e.g., water in both liquid and solid phases).

4. SOME THOUGHT ON OPTIMIZING ATTENUATION

The fraction T of electromagnetic radiation transmitted by

a cloud of particles is a product

$$T = \prod_j \exp(-\alpha_{vj} f_j z) \quad (32)$$

where α_{vj} is the volumetric attenuation coefficient of the j th kind of particle, f_j is the volume fraction in the cloud (the subscript j may denote composition, size, shape, or even orientation), and z is the cloud thickness. Equation (32) is a lower limit on the cloud transmission; T can be greater because of multiple scattering. The quantity $f_j z$ is the total volume of particles of the j th kind per unit area of the cloud.

Transmission can therefore be made arbitrarily low by increasing the mass of particles, which is effective but not efficient. To minimize the amount of material, one must maximize α_{vj} , and not merely over a narrow range of wavelengths. We can rewrite (32) as

$$-\ln T / fz = \sum_j \alpha_{vj} \bar{f}_j \quad (33)$$

where

$$f = \sum_j f_j, \quad \bar{f}_j = f_j / f, \quad \sum_j \bar{f}_j = 1.$$

So we want to maximize the sum on the right side of (33). I argued in the Introduction, that to do this by detailed calculations would be an endless task, even if all the analytical tools were at hand (which they are most definitely

not). Nevertheless, one can establish some bounds.

First, we can establish some practical lower bounds. The extinction cross section of any particle larger than the wavelength of the light illuminating it is approximately $2G$, regardless of its composition, where G is the geometrical cross sectional area of the particle projected onto the incident beam. G is proportional to some characteristic length d of the particle (for a sphere, its diameter). The volume of the particle is proportional to the cube of d . Thus, for such a particle

$$\alpha_v = C_{\text{ext}}/v = K/d, \quad (34)$$

where K is a constant depending on particle shape ($K = 3$ for a sphere). Let us take d to be of order $1 \mu\text{m}$, which gives α_v of order 10^4 cm^{-1} ; if d is ten times larger, then α_v is correspondingly less. Thus, $d \sim 1 \mu\text{m}$ is more or less the smallest size for which (34) is a good approximation for visible and near-visible wavelengths. It therefore seems that a volumetric attenuation coefficient of order 10^4 cm^{-1} represents a kind of lower bound: it is the value that can be obtained without making much of an effort. What is the upper bound?

According to the sum rule (27) integrated volumetric attenuation is independent of particle size. I argued in Sec. 3.1 that when a particle is illuminated by an electromagnetic wave, various electromagnetic modes may be excited. A specific example of this is provided by a sphere. The extinction cross

section of a sphere is given by the infinite series

$$C_{\text{ext}} = (2\pi/k^2) \text{Re}\{\sum (2n+1)(a_n + b_n)\} \quad (35)$$

Each coefficient corresponds to an electromagnetic mode of the sphere; a_n correspond to modes of electric type, b_n to modes of magnetic type. The larger the sphere, the more terms in (35) are needed for satisfactory convergence; that is, the larger the sphere, the more modes are excited by the incident wave. According to the sum rule (27), the integrated (volumetric) extinction is independent of particle size. Thus, the larger the particle, the more that a fixed amount of total extinction has to be shared by more modes. Conversely, the smaller the particle, the fewer the modes, hence the more extinction associated with each one of them. To make my point, I have invoked a sphere, but my conclusion is independent of particle shape.

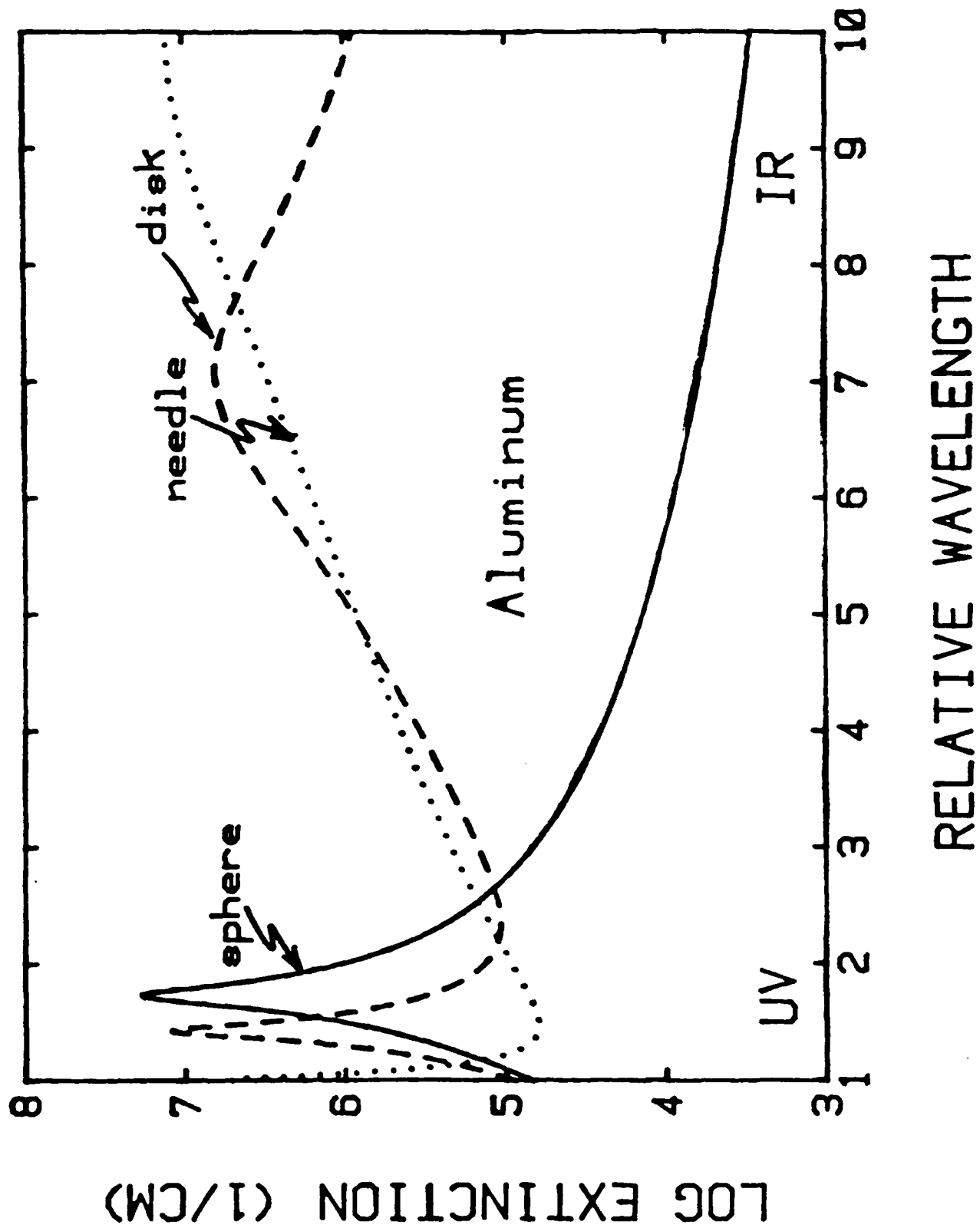
We therefore must look to small (compared with the wavelength) particles for the greatest possible extinction per unit volume. It follows from (27) and (29) that for a given shape, metallic particles will have the greatest integrated extinction. Moreover, it is the extreme shapes that gives (29) its greatest value. For a (perfectly sharp) needle or a (perfectly flat) disc, $L_1 = 0$, hence for these ideal particles integrated extinction is infinite.

To estimate the greatest possible volumetric extinction, I did some simple calculations for very small (compared with the

wavelengths of ultraviolet light) spheres and randomly oriented discs and needles of aluminum. Aluminum is almost an ideal free-electron metal; its dielectric function is given to good approximation by (12). I took the plasma frequency (in electron volts) to be 15 eV; the damping factor was 0.6 eV. The results are shown in Fig. 1. Note that the sphere gives the greatest peak extinction. This is not surprising in light of the sum rules. Fewer modes are excited in a sphere than in an asymmetric particle such as a needle or a disk. Peak extinction is about 10^7 cm^{-1} . I claim that this is a practical upper bound. Moreover, this bound cannot be obtained over a wide range of frequencies. A practical upper bound over at least one decade from the ultraviolet to the near infrared is 10^6 cm^{-1} , and this would have to be obtained with a mixture of particles having different shapes.

I argued at the beginning of this section that volumetric extinction of 10^4 cm^{-1} could be obtained with almost no thought. One could almost select particles at random. With a bit of thought it is possible to increase this number by a factor of 100. A further factor of ten increase might be possible, but this would likely be obtained at the expense of high extinction in one spectral region being paid for by much lower extinction in another.

Fig. 1 Volumetric extinction by aluminum particles that are small compared with the wavelengths of ultraviolet light.



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